

SEARCHING FOR ORGANICS PRESERVED IN 4.5 BILLION YEAR OLD SALT

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Introduction: Our understanding of early solar system fluids took a dramatic turn a decade ago with the discovery of fluid inclusion-bearing halite (NaCl) crystals in the matrix of two freshly fallen brecciated H chondrite falls, Monahans (1998, hereafter simply “Monahans”) (H5) and Zag (H3-6) [1, 2]. Both meteorites are regolith breccias, and contain xenolithic halite (and minor admixed sylvite – KCl, crystals in their regolith lithologies. The halites are purple to dark blue, due to the presence of color centers (electrons in anion vacancies) which slowly accumulated as ⁴⁰K (in sylvite) decayed over billions of years. The halites were dated by K-Ar, Rb-Sr and I-Xe systematics to be 4.5 billion years old [2-4]. The “blue” halites were a fantastic discovery for the following reasons: (1) Halite+sylvite can be dated (K is in sylvite and will substitute for Na in halite, Rb substitutes in halite for Na, and I substitutes for Cl). (2) The blue color is lost if the halite dissolves on Earth and reprecipitates (because the newly-formed halite has no color centers), so the color serves as a “freshness” or pristinity indicator. (3) Halite frequently contains aqueous fluid inclusions. (4) Halite contains no structural oxygen, carbon or hydrogen, making them ideal materials to measure these isotopic systems in any fluid inclusions. (5) It is possible to directly measure fluid inclusion formation temperatures, and thus directly measure the temperature of the mineralizing aqueous fluid [1].

In addition to these two ordinary chondrites halite grains have been reliably reported in several ureilites [5], an additional ordinary chondrite (Jilin) [6], and in the carbonaceous chondrite (Murchison) [7], although these reports were unfortunately not taken seriously. We have lately found additional fluid inclusions in carbonates in several additional carbonaceous chondrites. Meteoritic aqueous fluid inclusions are apparently relatively widespread in meteorites, though very small and thus difficult to analyze.

Isotopic Work: Last year we reported results of the first O and H isotopic measurements of the aqueous fluids present within the Monahans and Zag halites [8]. Variations of δD of the fluids range over $-330(90; 2\sigma)$ to $+1200(90)\text{‰}$ for Monahans and $-300(96)\text{‰}$ to $+90(98)\text{‰}$ for Zag. $\Delta 17O$ of the fluids range over $-16(22)\text{‰}$ to $+18(10)\text{‰}$ for Monahans and $+3(10)\text{‰}$ to $+27(11)\text{‰}$ for Zag. The variations are larger than the reproducibility of standard analyses and suggest that isotope equilibria were under way in the fluids before trapping into halite. The mean values of δD and $\Delta 17O$ are $+290\text{‰}$ and $+9\text{‰}$, respectively. The mean values and the variations of the fluids are different from the representative values of ordinary chondrites, supporting our view that the aqueous fluids were not indigenous to the H chondrite parent-asteroid(s) but rather were exogenous fluids delivered from somewhere else. The implication is that the halites travelled from another early solar system body (or bodies) that was (were) undergoing cryovolcanism. It is interesting that the aqueous fluid δD is intermediate in composition between primitive meteorites and Oort cloud comet coma water [8].

Organics: Simple organic structures such as nanoglobules are commonly present in astromaterials, even those that have been metamorphosed to a significant degree [9]. For example, they are present in CI chondrites which we know have been subjected to boiling aqueous fluids. Our previous work on the aqueous fluid inclusions in meteoritic halite has demonstrated that the fluids were never at temperatures greater than $\sim 25^\circ\text{C}$ – far lower than CI

chondrites, and more in line with most CM chondrites [1]. Terrestrial halite commonly contains trapped organic structures, which can be perfectly preserved for hundreds of millions of years at least (the record is 250 million years so far [10]). We thus investigated whether complex organic compounds and structures were trapped within the growing meteoritic halites alongside fluid inclusions (and in fact may have served as nucleation points for the fluid inclusions).

We have already found that the meteoritic halites have inclusions that fluoresce under short- and long-wave UV radiation which is the most sensitive test for the presence of potential organics (G. Cody, personal communication, 2009), although the fluorescing phases don't have to be organics. We therefore examined freshly-cleaved surfaces of meteoritic halite crystals for trapped organic compounds by confocal Raman Microscopy in Andrew Steele's Lab at the Carnegie Institution [11]. Examination of Monahans and Zag halite grains with Raman imaging reveals the presence of small (<10 μm), primarily metal grains with oxidation/hydroxylation products and minor phases inconsistent with H-chondrite mineralogy that must arise from the halite grains' originating body. The grains are generally subrounded and composed largely of metal, magnetite and another phase which is probably fine-grained lepidocrocite ($\text{FeO}(\text{OH})$). Identification of lepidocrocite carries an element of uncertainty at the time of this writing due to broad spectral features shared with clays and glassy phases, but in advance of data from other techniques the identification as lepidocrocite is reasonable given the inclusions' apparent history as largely metallic clasts altered by interaction with brine. Additional phases include forsteritic olivine ($\text{Fo}\approx 98$), pyroxenes, a feldspar grain with Raman spectral affinity to anorthoclase. We indeed identified organics in the halite as well, including macromolecular carbon (MMC). One inclusion features aliphatic material with Raman spectral features consistent with a mixture of short chain aliphatic compounds. Our search for organics is continuing to other halite grains, and the fluid inclusions within meteoritic carbonates.

Parent Bodies: The minerals and compounds discovered thus far within Monahans/Zag halites are indicative of an originating body at least partly composed of equilibrated igneous materials (high Fo olivine, possibly the metal) which was subjected to aqueous alteration (the halite parent brine) and containing a light organic component (the short-chain aliphatic compounds). Ultimately, this material was ejected from the originating body with little or no disruption, as evidenced with the presence of surviving fluid inclusions. An actively geysering body similar to modern Enceladus [12] is a reasonable analogue. Also, the originating body may have been in close proximity to the H chondrite parent in order to generate the number of halite grains seen in Monahans and Zag. Other candidates for Monahans/Zag halite parent body(ies) include a young Ceres with its possible liquid ocean or other similar C-, P- or D-class asteroids [13], and Main Belt comet(s) [14].

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